SIMS

The Production of Magnesium by the Electrolysis of its Fused Salts

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THE PRODUCTION OF MAGNESIUM
BY THE
ELECTROLYSIS OF ITS FUSED SALTS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Clarence Edgar Sims

ENTITLED The production of magnesium by the electrolysis of its fused salts

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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INTRODUCTION AND HISTORY

Magnesium[8*] was first produced electrolytically by Bunsen by the electrolysis of fused anhydrous $MgCl_2$. Numerous attempts to produce it by reduction with carbon have all failed; magnesium carbide being formed in every case. Since Bunsen did his electrolysis a great deal of work by many different investigators has been done on the electrochemical preparation of magnesium. Unfortunately, the results of most of this work have been closely guarded so that very little information is available. Electrochemical industries have progressed wonderfully until the alkalie metals, aluminium and other metals with high solution tension are produced commercially in large quantities and by comparatively simple processes. But magnesium still presents a problem and to anyone who tries to make it in the laboratory it is evident

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*Note: The number refers to reference 8 in the Bibliography.

that there are a great many things involved which are not known or understood by persons outside of the plants where it is made. From the descriptions published in text books the production of magnesium would seem to be a simple thing, but judging from the work of various investigators, a good deal of the information in text books is merely assumed, without any knowledge of its authenticity. There are, however, some notable points on which most authors agree, and also, some important points on which they differ.

$MgCl_2$ crystalizes with 6 molecules of water and is very deliquescent. When an attempt is made to dehydrate $MgCl. 6 H_2O$ hydrolysis takes place to a large extent, HCl being given off, leaving MgO. For this reason it can not be used alone in the preparation of magnesium[6]. However, if a mixture of molecular proportions of $MgCl_2.6 H_2O$ and KCl, such as is found in the mineral carnallite, are fused the magnesium chloride is much more stable, although even then great difficulty is experienced in preventing decomposition. The addition of NH_4Cl to the fusion has a strong influence in preventing hydrolysis. Most investigators have used carnallite as a raw material but Tucker and Jouard[15] in their work declare it unsuitable for use and that an artificial mixture must be made. Oettel[3], nevertheless, used carnallite and gives some of the following directions and precautions. In melting down the salt in a gas flame care must be exercised so that the products of combustion do not get to the melt or water will be absorbed, forming an oxychloride which is decomposed by the current into hydrogen, chlorine, and MgO.

Sulphates are always present in carnallite to a greater or less extent. Magnesium sulphate dissolves in the melt and as

soon as any metal is formed reacts thus:

$$MgSO_4 + Mg \longrightarrow 2\ MgO + SO_2$$

The fine dustlike MgO forms a coating around the small globules of magnesium and effectively prevents them from coalescing. In all cases of the electrolysis of $MgCl_2$ the magnesium is widely scattered in small particles all through the melt. According to Oettel this is always due to a coating of MgO. The addition of CaF_2 in small amounts has a good influence in aiding the aggregation of the small globules. CaF_2 has a solvent action on MgO, although it doubtless helps also by lowering the surface tension of the magnesium. Stirring the hot melt before electrolysis with a carbon rod or adding sugar, flour, or any other reducing material will break up the sulphates.

$$MgSO_4 + C = MgO + CO + SO_2.$$

Another impurity which causes trouble is iron chloride which is alternately oxidized and reduced, thus using up a great deal of current. Lorenz[6] used a salt mixture of $MgCl_2 \cdot 6\ H_2O \cdot KCl \cdot NaCl$. This he electrolysed in an iron crucible which was used as the cathode, and obtained results for which he claims 70 percent current efficiency.

Seward and Von Kügelgen[17] have taken out a number of patents wherein other salts than $MgCl_2$ and KCl are used. In fact, so many patents are being taken out which specify the use of other salts that it is very evident that many investigators are having trouble with $MgCl_2$. Practically all the $MgCl_2$ occurs in carnallite which is obtained from the Stassfurt deposits in Germany. This supply is limited and carnallite is even now rather expensive. The process of dehydrating it is at the very best a slow, tedious,

and expensive one. After dehydrating it must be kept from moist air or decomposition will take place. In spite of extraordinary precautions[16] MgO will be formed which will make it difficult and often impossible to recover the greater portion of magnesium produced during an electrolysis. On the other hand magnesium occurs in large quantities in other forms than the chloride, and there seems no reason to doubt that methods could be worked up by which it could be produced more economically than from $MgCl_2$. The object, then, of this thesis was to endeavor to produce magnesium electrolytically, and in so doing to observe the phenomena in an effort to clear up some of the difficulties in the way of its production. Although some valuable information was obtained from the literature, most of it was so vague, uncertain, and, moreover, conflicting, that most of the work was pioneer work, as far as the author is concerned.

EXPERIMENTAL

Electrolytic Cell. Before any electrolysis could be done it was logically necessary to build a suitable apparatus for fusing and electrolysing the salt. As it turned out, by far the greatest amount of time was spent in designing, building, and revising this apparatus. However, the problem of dehydrating, fusing, and keeping the salt molten during electrolysis is probably as big a problem as any.

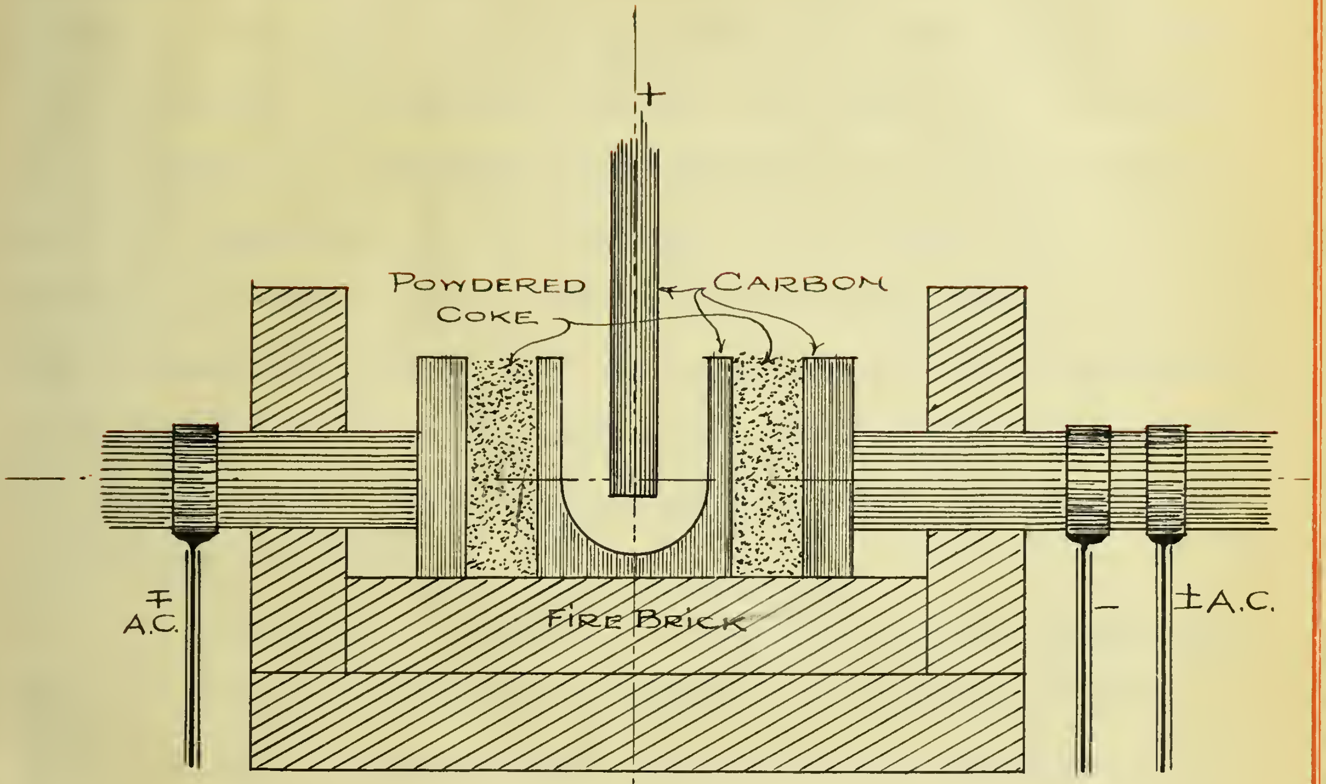
First a large iron crucible was tried, it being used as a cathode. A gas flame was used to heat it, but it was found that a blast lamp was necessary to obtain a high enough temperature. Even then the heating was so uneven that parts would be cold while the rest were too hot. The crucible was enclosed in bricks so as to form a sort of oven around it. Still the heating was unsatisfactory and it was difficult to keep the products of combustion from the melt. Moreover, the iron oxidized rapidly, scaled off the outside and dissolved in the slag from the inside, turning it green and viscous. The iron crucible and gas flame were both given up as unfeasible.

Then a graphite crucible was made by hollowing out a three inch graphite electrode. This was packed in heat-retaining asbestos in a small box made of fire-brick. The bottom of the crucible was connected with the outside by a carbon plate which served to conduct the current. The crucible itself was the cathode. The anode was lowered in at the top and consisted of a graphite rod. The circuit was arranged so that either alternating or

direct current could be sent through the circuit. The first attempt to melt the salt in it was by means of the heat caused by resistance of a thin graphite rod placed between the crucible bottom and the anode and through which alternating current was sent. The rod rapidly disintegrated, broke the circuit and allowed the melt to freeze before it had melted but very little. Then an arc was used to melt the salt. This was more successful. Because of the intense heat the arc was used only to start the fusion, the electrode being then dipped into the melt and the resistance of the molten salt to the alternating current finished the fusion. At this point the alternating current was switched off and the direct current switched on. However, only a storage battery was available at this time for direct current, and the small current that could be drawn from it proved entirely insufficient to keep the salt molten.

Later a 10 K.W. direct current generator was made available for direct current. This was capable of giving only fifteen to sixteen volts but was rated at over eight hundred amperes. Efforts were made to use a direct current arc but owing to the low voltage a stable arc could not be maintained.

Having worked with resistance furnaces, the idea was entertained that a core of granular carbon such as is used in a carborundum furnace would be excellent to heat up a crucible. Frary's[16] article on the formation of a magnesium sub-oxide was very useful here. He heated up his crucible and melted his salt by imbedding it in crushed coke through which he sent a large alternating current to melt the salt and then a smaller one to



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keep up the temperature. Acting on this idea the furnace shown in the accompanying drawing was constructed. The crucible is 4" X 4½" outside dimensions and 3" X 3½" inside dimensions. It is imbedded in a core of granular coke. At the ends of the core are graphite plates which are connected with two-inch square graphite electrodes. Alternating current is sent between these electrodes and the resistance of the core heats up the crucible very quickly. By regulating the voltage of the alternating current the temperature of the core may be regulated. The anode is lowered into the crucible, and the cathode connection is made on one of the electrodes so that the direct current for electrolysis is superimposed on the alternating current circuit. To carry off the gases formed a hood was constructed. This furnace came up to all expectations.

Preparation of Melt. The salt used was carnallite from the Stassfurt deposits in Germany. It contained a small amount of iron and approximately ten percent of sulphate. No attempt was made to purify it except to break up the sulphates during fusion with argols or carbon. At first a porcelaine casserole was used to fuse down the carnallite and make the anhydrous salt. Ammonium chloride was added during all dehydration operations to prevent hydrolysis of the $MgCl_2 \cdot 6\ H_2O$. For this reason it had to be done under a hood for the NH_4Cl fumes came off in clouds. A gas blast lamp was the only available means of heating the casserole, and as explained before a blast lamp is very unsatisfactory because it heats such a small area at a time. Also, the casseroles cracked after short use. By this method a great amount of time was spent in obtaining relatively small amounts of

the anhydrous salt.

When the final electrolysis cell was constructed, however, the carnallite and ammonium chloride was put directly into the crucible and dehydrated by the heat of the alternating current. This method was quick and efficient. In thiscase the red hot graphite crucible was sufficient to break up the sulphates present. It was noticed that if the carnallite was fused at a rather low temperature water would be given off and the mass would melt down to a clear liquid, which on being raised to a certain temperature would suddenly foam up and boil over the sides of the crucible. What was left in the crucible would then settle down to a clear red hot liquid. The only way this could be explained was that most of the water is given up readily but that it takes a higher temperature to expel the last traces. When the salt is raised to this temperature it all comes off at once. To avoid this small amounts were added at a time and these completely dehydrated before any more was put in.

Electrolysis. The first runs were made at as low a temperature as the salt could be kept molten. It is rather viscous at this temperature and the resistance is high so that with the low voltage the current was necessarily low. With twelve volts and the anode nearly touching the bottom of the crucible, not more than fifteen amperes could be forced through. These runs lasted about two hours but in no one was even a trace of metal found. However, a great deal of oxide was found in the melt at the finish. About five percent of CaF_2 was used in all runs.

The next set of runs were made at a low red heat and from twenty to twenty-five amperes. Under these conditions the

electrolysis appeared to progress quietly and favorably, but after running for from an hour to an hour and a half no metal could be found in the melt.

The electrolysing current was not sufficient to keep the salt molten and the alternating current was run continuously through-out the electrolysis.

The third series of runs was made at a bright red heat (about 900° C). In these as high a current as possible was forced through the cell. At the beginning of the electrolysis a current of from seventy to eighty amperes was obtained but as it progressed the current gradually fell until only forty to fifty amperes could be obtained. Accumulations of solid matter (mainly MgO) were found on the bottom and sides of the crucible after the electrolysis, and these are supposed to be the cause of the falling off of the current. In each of these cases the presence of metallic magnesium was very apparent, although it was widely disseminted throughout the melt and was not recovered.

The different runs in each series were so nearly alike that one description fits them all. It was thought that if ammonium chloride was added during the electrolysis that the decomposition of the $MgCl_2$ would be prevented, but the evolution of the vapor stirred up the melt so much that it was considered impracticable after a trial.

After electrolysis, quantities of a black solid substance were found in the melt. These reacted with water in the cold, and gave off a gas which was apparently hydrogen. This agrees very well with Frary's[16] results in which he proves this substance to be a sub-oxide of magnesium formed during the elec-

trolysis of magnesium potassium chloride when magnesium oxide is present.

Other Salts. During the first part of the work a great deal of time was spent in an effort to find a suitable solvent for MgO. The idea was to electrolyse the MgO in a manner analogous to the electrolysis of Al_2O_3 dissolved in cryalite. According to Lodge's "Notes on Assaying", twenty parts of borax will dissolve and make fluid six parts of MgO. This was found to be true only at a temperature causing mixing of anode and cathode products. Then a number of mixtures were tried. Of course anything containing a metal with a lower solution tension than magnesium could not be used. The following composition or rather mixture seemed to give the best results: Borax glass, four parts; calcium fluoride, one part; sodium fluoride, one part; sodium carbonate, two parts. This will dissolve and make fluid one part of MgO at a bright red heat. Cryolite appears to have a solvent action on MgO. Owing to lack of time no runs were made on any of these mixtures after an efficient furnace was built.

CONCLUSIONS

Unfortunately the work had to be left off, because of lack of time, just as it was well begun. The electrolysis of fused salts in general is a difficult and elusive problem and one about which comparatively little is known. A few methods, the essential details of which are kept secret, are really successful in producing pure metal. Operations that appear in text books as being very simple are in reality very complex and have baffled completely some of our best chemists who have sought to investigate them. One characteristic that delays progress in this field is the small part that analogy plays. The fact that a certain procedure with one salt gives the pure metal, affords no clew whatsoever to the method which will be successful in the case of another salt. A few illustrations will help make this statement clear. Calcium and magnesium are two metals very much alike in their physical and chemical properties. In fact, so nearly alike are they in their chemical properties that one of the problems in analysis is their complete separation. Still $CaCl_2 . 6 H_2O$ may be dehydrated and fused pure without hydrolysis while $MgCl_2 . 6 H_2O$ even when mixed with KCl and NH_4Cl is fused only with great difficulty without hydrolysis. Fused calcium chloride will dissolve CaO and $CaCO_3$ which are readily changed to the chloride when dry HCl is passed in. MgO is practically insoluble in fused $MgCl_2$ and is not acted on in the least by hot dry HCl. The method, then, for the production of each different metal must be worked out in-

dividually and without precedence to go by. And anyone who attempts an investigation in this field soon realizes that much preliminary experimenting is necessary before any actual work may be done.

The present investigation seems to indicate several things. First, the carnallite must be heated quite a bit above its melting temperature to drive out the last traces of water. It is advisable to add the carnallite in small portions and completely dehydrate each portion before the next is added. It must be heated to a bright red heat in order to decompose the sulphate present.

Secondly, during electrolysis the melt should be kept at a dull red heat to obtain the best results. If the temperature is too low the melt is too viscous and if the temperature is too high the magnesium chloride volatilizes very readily.

The current density should be very high for best results. About one hundred amperes per square dm. should give favorable results. It seems certain that if a higher current could have been run in the last series of experiments that the metallic magnesium would have been obtained in quantities so that it could be recovered. So convincing are the indications, the intention is to make some more runs in the near future with modifications so that a higher current may be used.

It seems reasonable and the investigations would lead us to believe that a suitable solvent may be found for MgO in which it could be electrolysed to form metallic magnesium.

I will here take advantage of the opportunity to thank Dr. Mac Innes for his timely suggestions and sympathetic interest in the investigation.

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